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OXY- AND THIO- PHOSPHORUS ACID DERIVATIVES OF TIN. III. THE X-R--ETC(U)
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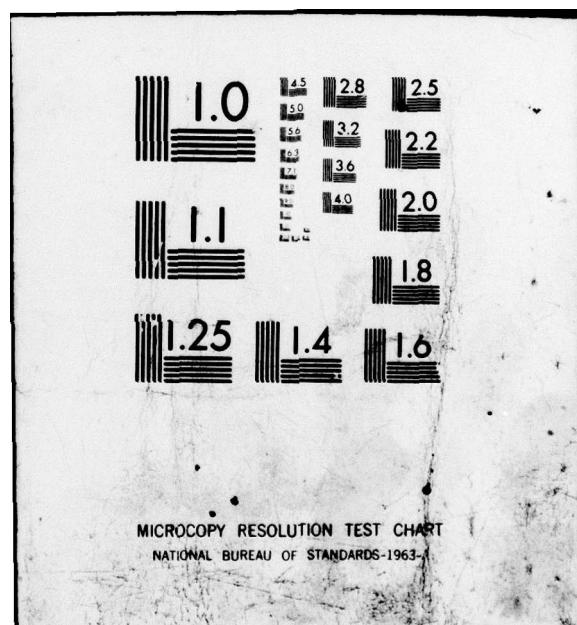
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⑥ Oxy- and Thio- Phosphorus Acid Derivatives of Tin. III.
The X-ray Crystal and Molecular Structure of Bis-(σ, σ' -
-Diphenyldithiophosphato)tin(II), $\text{Sn}(\text{S}_2\text{P}(\sigma\text{C}_6\text{H}_5)_2)_2$, a
Bicyclic Dimer Held Together by $\text{h}^6\text{-C}_6\text{H}_5$ to Tin(II) Interactions

by

⑩ M.B. Hossain, J.L. Lefferts, K.C. Molloy, D. van der Helm
and J.J. Zuckerman

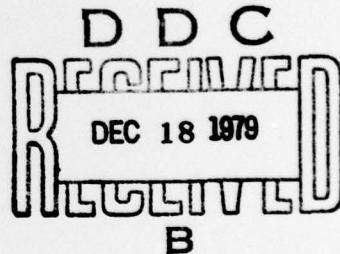
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20. ABSTRACT (Continue on reverse side if necessary and identify by block number) Bio-[O,O' -diphenyldithiophosphato]tin(II), $\text{C}_{24}\text{H}_{20}\text{O}_4\text{P}_2\text{S}_4\text{Sn}$ crystallizes in the triclinic space group PI with $a=10.499(5)$, $b=13.948(7)$, $c=9.291(4)\text{A}$; $\alpha=99.18(6)$, $\beta=95.71(5)^\circ$, $\gamma=91.80(5)^\circ$. The structure was studied by Monochromated Mo-K radiation and refined to a final R value of 2.9% for 5517 reflections. The centrosymmetric, dimer contains one ligand bridging two tin atoms intermolecularly while simultaneously chelating one tin atom in an extremely anisobidentate manner. A planar Sn_2S_2 four-membered ring is circumscribed by an $(\text{SnSPS})_2$		

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eight-membered ring. The dimer is in addition held together by a long π -interaction of 3.46 Å along a S-Sn vector to be the center of one of the aromatic rings of an ester group of the bridging ligand of the second monomeric unit. This ring is oriented in a spatially significant position perpendicular to the assumed vector of the tin lone pair producing a distorted octahedral (4-6) geometry at the metal center, and the sole example of a $\text{h}^6\text{-C}_6\text{H}_5$ main group π -bond known, especially one contributing to the formation of a dimer.

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Oxy- and Thio- Phosphorus Acid Derivatives of Tin. III.

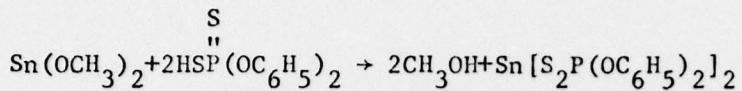
The X-ray Crystal and Molecular Structure of Bis-[0,0'-Diphenyldithiophosphato]tin(II), $\text{Sn}[\text{S}_2\text{P}(\text{OC}_6\text{H}_5)_2]_2$, a Bicyclic Dimer Held Together by $\underline{\text{h}}^6\text{-C}_6\text{H}_5$ to Tin(II) Interactions [**]

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The tin(II) dithiophosphate ester $\text{Sn}[\text{S}_2\text{P}(\text{OC}_6\text{H}_5)_2]_2$ (m.p. 125.5-126.5°C) has been synthesized by the reaction of dimethoxytin(II) with two equivalents of 0,0'-diphenyldithiophosphoric acid in benzene:



and characterized by ^{119}Sn Mössbauer [I.S.=3.78±0.02; Q.S.=1.06±0.04mm/s] and mass [highest observed m/e=682(2.9%)M⁺] spectroscopies as well as micro-analyses [Found: C, 42.50; H, 3.10%. Calc'd. for $\text{C}_{24}\text{H}_{20}\text{O}_4\text{P}_2\text{S}_4\text{Sn}$: C, 42.31; H, 2.96%]. A triclinic single crystal of space group $\overline{\text{P}1}$ [$a=10.499(5)$, $b=13.948(7)$, $c=9.291(4)\text{\AA}$; $\alpha=99.18(6)^\circ$, $\beta=95.71(5)^\circ$, $\gamma=91.80(5)^\circ$] was studied by Mo-K_α X-radiation and refined to a final R value of 2.9% for 5517 reflections.

The centrosymmetric dimer shown in Fig. 1 contains one ligand bridging two tin atoms intermolecularly while simultaneously chelating one tin atom in an extremely anisobidentate fashion, via the three-coordinated (S4). A second ligand is involved in normal anisobidentate chelation as is found in the tin(II) dithiocarbamate, $\text{Sn}[\text{S}_2\text{CN}(\text{C}_2\text{H}_5)_2]_2$ ^[1] and dithiocarbonate, $\text{Sn}[\text{S}_2\text{COCH}_3]_2$.^[2] A planar Sn_2S_2 four membered ring such as is found in Sn_2S_3 ^[3] and $(\text{CH}_3\text{Sn})_4\text{S}_6$ ^[4] is circumscribed by an $[\text{SnSPS}]_2$ eight-membered ring in an arrangement reminiscent of the eight-membered centrosymmetric rings formed by the tin(IV) atoms and dichlorophosphate groups in the dimeric $[\text{Cl}_3\text{SnPO}_2\text{Cl}_2 \cdot \text{POCl}_3]_2$.^[5] Our structure contrasts with those adopted by lead(II) diethyldithiophosphate in which the metal atoms are chelated in monomers^[6], and its diisopropyl analogue in which the metal atom is coordinated by six sulfur atoms, two of which bonded intermolecularly to give a polymeric lattice^[7].

Unlike these structures, the dimeric title compound is held together by two coordinate bonds at 3.0248(7) emanating from S(4) or S(4') atoms plus a long π -interaction at 3.46 \AA along the S(3)-Sn vector to the center of one of the aromatic rings of an ester group of the bridging ligand of the second monomeric unit. This ring is oriented in a spatially significant position perpendicular to the assumed vector of the tin lone pair producing a distorted octahedral (ψ -6) geometry at the metal center. π -Interactions with tin(II) lone pairs are found in $\underline{h}^6\text{C}_6\text{H}_6\text{Sn}(\text{AlCl}_4)_2\cdot\text{C}_6\text{H}_6$ ^[8-10] and $\underline{h}^6\text{C}_6\text{H}_6\text{SnCl}(\text{AlCl}_4)$ ^[11-12] where the distances to the center of the rings lie in the range 2.74 to 2.90 \AA , long with respect to transition metal-arene distances. Our dimer is unique however, for two reasons. Firstly, to our knowledge^[13] we have here the only example of an $\underline{h}^6\text{C}_6\text{H}_5$ main group π -bond; and secondly, the only known example of such an interaction contributing to the formation of a dimer from the constituent monomers.

The existence of the Sn_2S_2 ring is confirmed on close inspection of the phosphorus-sulfur distances. The more tightly bound to a metal the dithiophosphate sulfur is, then the longer its bond to phosphorus.^[14] For example, in the purely chelating ligands in our structure atom S(1) makes a short tin bond [S(1)-Sn(1)=2.6230(6)] and a long bond to phosphorus [S(1)-P(1)=2.0016(8) \AA]. Atom S(2) does the opposite [S(2)-Sn(1)=2.8300(6); S(2)-P(1)=1.9670(8) \AA]. Thus we conclude that atom S(2) is double-bonded to P(1). However, comparison of the two ligands bonded to each tin atom reveals that although the bridging sulfur-tin bond is significantly longer [S(4)-Sn(1)=3.0248(7)] than the corresponding chelating bond [S(2)-Sn(1)=2.8300(6)], the presumably P=S distances are quite similar [P(2)=S(4)=1.9636(8); P(1)=S(2)=1.9670(8) \AA]. This unexpectedly long P(2)=S(4) distance must arise because of the electron withdrawal along the S(4)-Sn(1) vector at 3.3914(6) \AA , thus confirming the interaction between these two atoms. In $[\text{CuS}_2\text{P}(\text{OC}_3\text{H}_7\text{-iso})_3]_4$, on the other hand, the three-

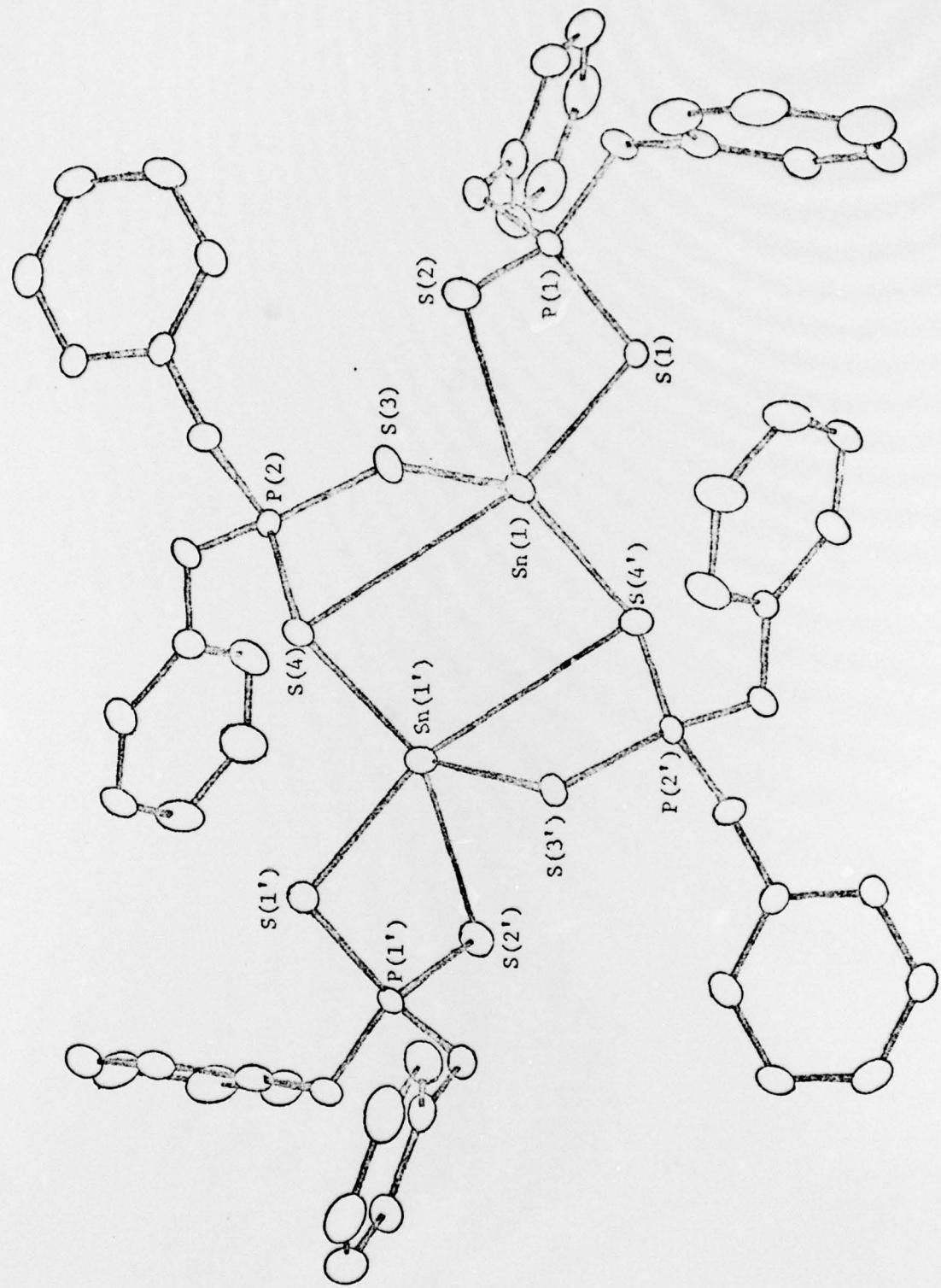
coordinated sulfur atoms that bridge two metal centers form equal or stronger sulfur-metal bonds than the sulfurs bonded to only one metal atom. In that case electron withdrawal from the bridging sulfur-phosphorus P=S bond so lengthens this distance that it actually becomes longer than the adjacent P-S single bond.^[15]

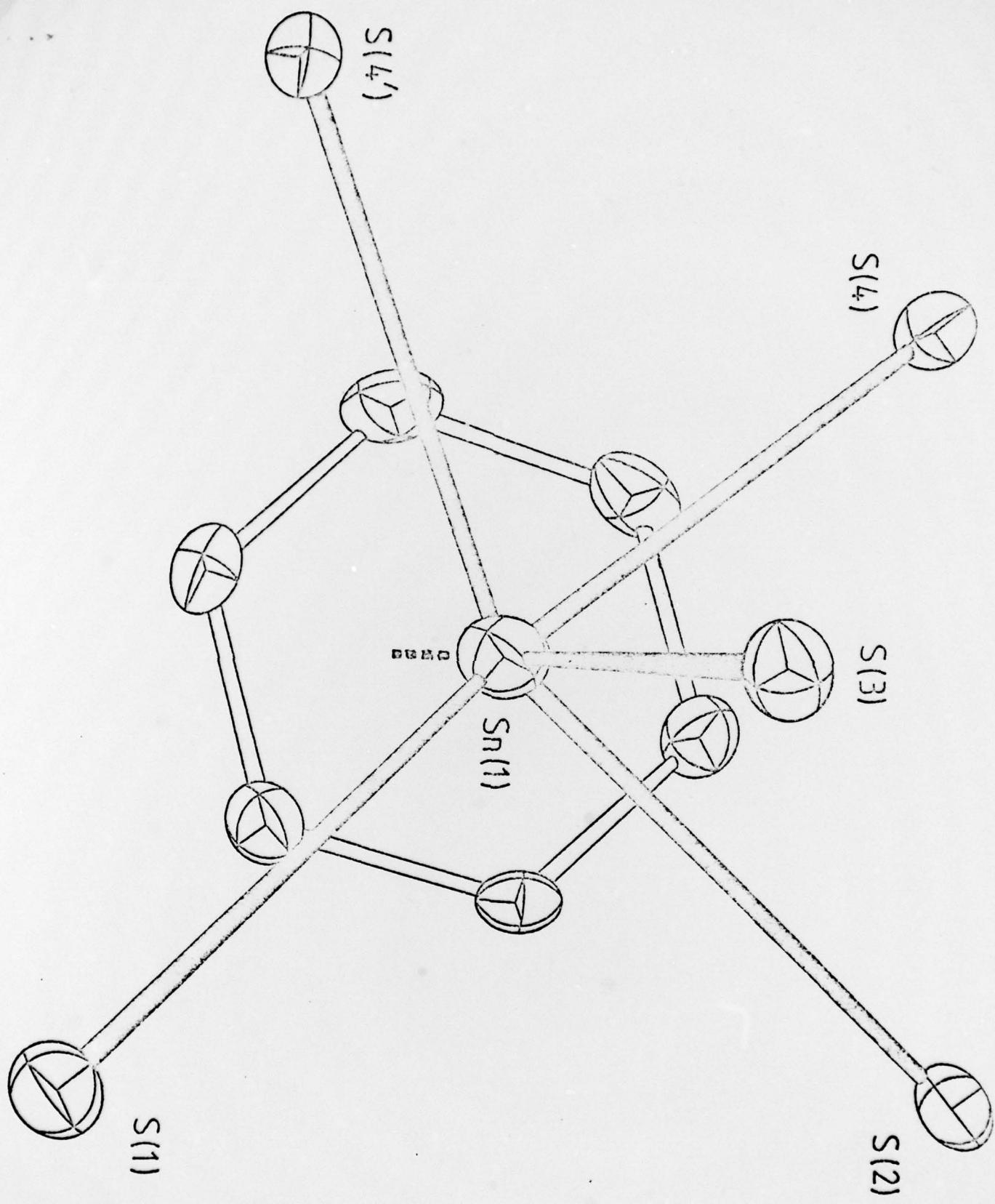
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Figure Captions

Fig. 1. The dimeric molecular structure of bis-[0,0'diphenyldithiophosphato]tin(II), $\text{Sn}^{\text{II}}[\text{S}_2\text{P}(\text{OC}_6\text{H}_5)_2]_2$, held together by bifurcated, three-coordinated, sulfur atom bonds and $\underline{\text{h}}^6-\text{C}_6\text{H}_5$ interactions with the tin(II) lone electron pairs.

Fig. 2. The $\underline{\text{h}}^6-\text{C}_6\text{H}_5$ -tin(II) vector. The distance to the center of the ring is 3.46A.





80